

# Complex System of Poly(methacrylic acid) with Poly(vinylpyrrolidone) in Aqueous Media

Shuyang Liu, Mingjiao Yang, Yi Dan

State Key Laboratory of Polymer Materials Engineering, Polymer Research Institute, Sichuan University, Chengdu 610065, China

Received 10 October 2003; accepted 20 May 2004

DOI 10.1002/app.20991

Published online in Wiley InterScience (www.interscience.wiley.com).

**ABSTRACT:** Two-component polymer solutions [i.e., poly(methacrylic acid) (PMAA) and poly(vinylpyrrolidone) (PVP)] were prepared through solution polymerization. The complex system PMAA/PVP was obtained through the mixing of a PMAA solution and a PVP solution in different volume ratios at certain concentrations. The properties of the component solutions and the complex system were investigated with transmittance, surface tension, and viscosity

measurements. The results showed that the properties of the complex system were related not only to the ratio of PMAA to PVP but also to the concentration of the PMAA and PVP solutions. © 2005 Wiley Periodicals, Inc. *J Appl Polym Sci* 96: 2280–2286, 2005

**Key words:** mixing; solution properties; viscosity

## INTRODUCTION

Poly(vinylpyrrolidone) (PVP) contains acrylamide and carbonyl groups and so can interact with some polar compounds to form new materials with special performances. The complexation of PVP with micro-molecules has been studied in depth,<sup>1</sup> and this complex system is widely used in our daily lives. PVP can also interact with some polymers containing polar groups to modify the properties of the polymers.

The interactions of PVP with hydrolyzed polyacrylamide (HPAM), polyimide (PI), and poly(methacrylic acid) (PMAA) are described in the relevant literature.<sup>2–8</sup> Yang and Xu,<sup>2</sup> for example, researched the mixed system PVP/HPAM with viscosity, ultraviolet (UV) spectroscopy, infrared, and differential scanning calorimetry (DSC) measurements, and the results showed that the interaction of PVP and HPAM could result in the formation of a supermolecular structure, and the viscosity resistant to salt could be enhanced. Yuan and Wu<sup>3</sup> researched molecular composites of PI and PVP, and the specific acid–base interaction between the polyamic acid (the precursor of PI) and PVP was confirmed experimentally; by this specific interaction, the miscibility of PI with PVP was substantially improved. Yang et al.<sup>4</sup> studied the mechanism of complexation between hydroxy ethyl cellulose (HEC) and

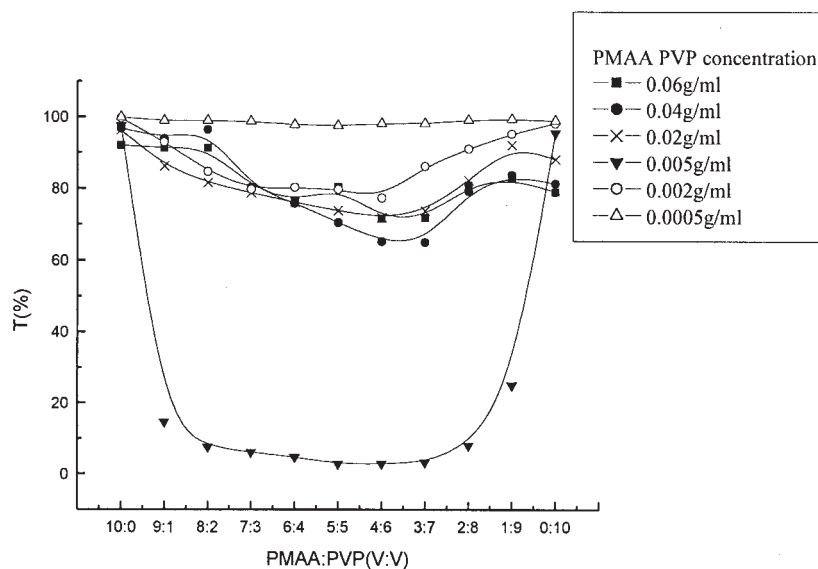
PVP with viscosity, UV, Fourier transform infrared (FTIR), and DSC methods. The results indicated that the viscosity of PVP/HEC complex systems displayed negative synergic effects, and both the UV and FTIR spectra showed that the PVP/HEC complex was formed through hydrogen bonding.

PMAA is a low-cost and widely used polymer. It contains carboxyl groups that can interact well with PVP to form a new compound material. While researching PMAA/PVP complexation, Peng and Yu<sup>5</sup> discovered that PMAA/PVP complexation could absorb the hydroxybenzene substance well and could be used in water treatment. In addition, Liu et al.<sup>6</sup> researched PMAA/PVP complexation with a fluorescence technique, and the results showed that the conformation of PMAA molecular chains changed after the complexation of PMAA with PVP. Cascone et al.<sup>7</sup> prepared PMAA/PVP complexes by template and direct-mixing methods, and they studied the properties with DSC, thermogravimetric analysis, and FTIR measurements. The results showed that the complexes prepared by the template method presented a more regular structure than those made by direct mixing. Kazakhstan's scientists studied the surface properties of PMA/PVP complexes.<sup>8</sup> All this research was mostly concerned with solid complexes formed by the mixing of PMAA and PVP solutions; studies on the PMAA/PVP complex system in aqueous media are rarely reported.

Because PMAA and PVP, as well as their corresponding monomers, are water-soluble, they can be prepared by solution polymerization in aqueous media, which are much better than other media because

Correspondence to: Y. Dan (liushuyang.student@sina.com).

Contract grant sponsor: National Natural Science Foundation of China; contract grant number: 29974021.



**Figure 1** Variation of the transmittance of the complex system PMAA/PVP with the volume ratio at certain concentrations.

of environmental factors. Therefore, we prepared PMAA and PVP by solution polymerization in aqueous media and mixed PMAA and PVP solutions to obtain the complex system PMAA/PVP. We then researched the interaction between the macromolecular chains in aqueous media. In this study, we examined the interaction of PMAA and PVP with transmittance, surface tension, and viscosity measurements.

## EXPERIMENTAL

### Materials

Vinyl pyrrolidone (NVP; 99% content) was supplied by Beijing Oilfield Chemical Co. (Hangzhou, China).  $\alpha$ -Methylacrylic acid (MAA; chemically pure) was a product of Chengdu Kelong Chemical Reagents Factory (Chengdu, China). Azobisisobutyronitrile (AIBN) and potassium persulfate (KPS), from Beijing Chemical Factory (Beijing, China), were chemically and analytically pure, respectively. All the materials were used directly. Deionized water was used in all experiments.

### Preparation of PVP

PVP was prepared by solution polymerization in an aqueous medium. The initiator (AIBN; 0.012 g), 16 g of NVP, and 4 g of deionized water were added to a three-necked flask (TNF) equipped with a mechanical stirrer and a reflux condenser. When the temperature of the mixture rose to 70°C, the temperature was kept constant for about 3 h. The obtained PVP solution was dried at 100°C for about 3 h, and a PVP solid was obtained.

### Preparation of PMAA

PMAA was also prepared by solution polymerization in an aqueous medium. The initiator (KPS; 0.075 g), 15 g of MAA, and 135 g of deionized water were added to a TNF equipped with a mechanical stirrer and a reflux condenser. When the temperature of the mixture rose to 80°C, the temperature was kept constant for about 5 h. The obtained PMAA solution was dried for about 3 h, and a PMAA solid was obtained.

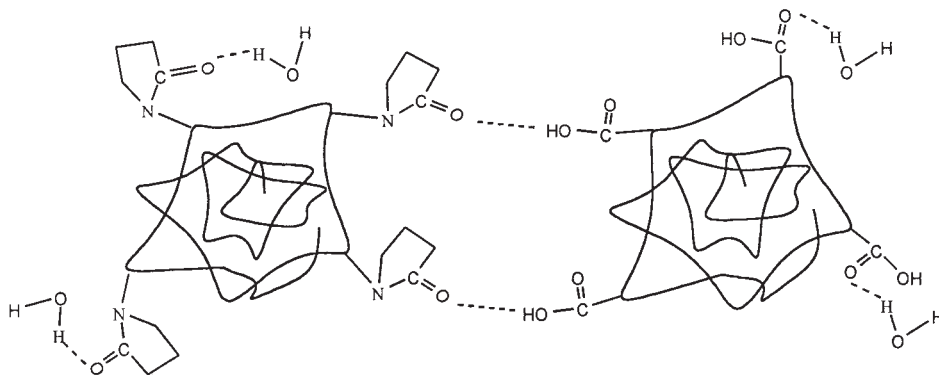
### Preparation of the complex system PMAA/PVP

The solid PVP and PMAA were solved in deionized water; the concentrations were 0.06, 0.04, 0.02, 0.005, 0.002, and 0.0005 g/mL. Then, PMAA and PVP solutions of certain concentrations were mixed in different volume ratios. In the end, the complex system PMAA/PVP was obtained. The volume ratio of the PMAA solution to the PVP solution ranged from 9:1 to 1:9.

### Measurements

Transmittance measurements of the complex system PMAA/PVP were performed on a model 721 photometer (Sichuan Analytical Apparatus Factory, Chongqing, China) at room temperature. The wavelength was 500 nm. The reference solution was deionized water, the transmittance of which was determined to be 100%.

Surface tension measurements of the complex system PMAA/PVP were performed on an interface tension apparatus (Hebei Province Chende Material Test-Machine Factory, Chende, China) at room tempera-



**Scheme 1** Complexation of PMMA and PVP at high concentrations.

ture. Deionized water was the reference solution, the surface tension of which was determined to be  $73 \pm 0.2$  mN/m.

Viscosity measurements of the complex system PMAA/PVP were performed on a Brookfield LVDV-III viscometer (Brookfield Engineering Laboratories, Inc., Middleboro, MA) at  $25 \pm 2^\circ\text{C}$ .

## RESULTS AND DISCUSSIONS

According to the experiments, when PMAA and PVP solutions were mixed in different concentrations, the macrophenomenon of complexation was markedly different. When the concentrations of the component solutions were 0.06, 0.04, and 0.02 g/mL, achromic and transparent aqueous gels with small, white floccules were obtained. When they were mixed at the medium concentration, that is, 0.005 g/mL, strange phenomena occurred: lots of small, white floccules were obtained, and the complex system became opaque. When they were mixed at the lower concentration, that is, 0.002 mL/g, a transparent and azury solution was obtained. When the concentration of the component solution was 0.0005 g/mL, the complex

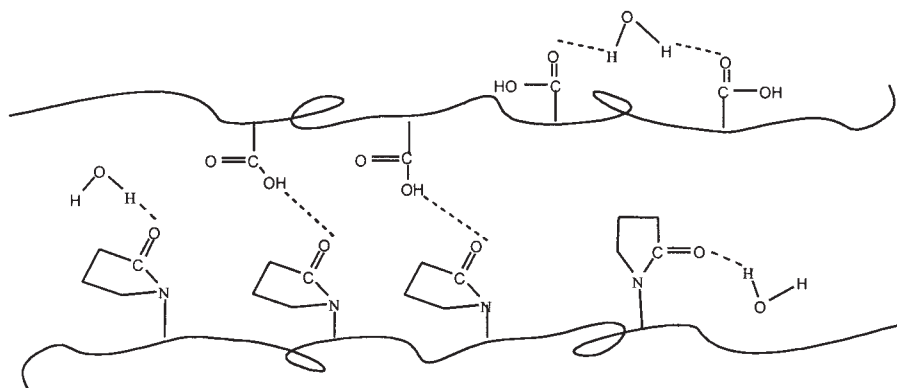
system remained in the achromic and transparent solution state.

When PMAA and PVP solutions of certain concentrations were mixed in different volume ratios, the phenomenon of the complex system was also different. At the higher and medium concentrations (0.06–0.005 g/mL), when the volume ratio of PMAA to PVP was 6:4 to 3:7, more aqueous gel or white floccules could be gained than with other volume ratios.

From the variations of the phenomena of the complex system, we assumed that PMAA and PVP interacted by hydrogen bonds. Intermacromolecular complexation caused the properties of the complex system to be much different from those of the component solutions. Therefore, we investigated the transmittance, surface tension, and viscosity of the complex system and component solutions to determine the variation rules.

### Analysis of the transmittance of the complex system PMAA/PVP

Figure 1 shows the variation of the transmittance of the complex system with the volume ratio of PMAA to



**Scheme 2** Complexation of PMMA and PVP at low concentrations.

TABLE I  
Volume Ratios and Group Molar Ratios of the Complex System

PMAA/PVP (volume ratio)	9:1	8:2	7:3	6:4	5:5	4:6	3:7	2:8	1:9
—COOH/C=O (molar ratio)	11.6:1	5.16:1	3.01:1	1.93:1	1.29:1	0.86:1	0.55:1	0.32:1	0.14:1

PVP when the concentrations of the component solutions were 0.0005, 0.002, 0.005, 0.02, 0.04, and 0.06 g/mL. At a lower concentration, that is, 0.0005 g/mL, the transmittance of the complex system was nearly the same as that of the component solutions in the range of 9:1 to 1:9 PMAA/PVP. When the concentration of PMAA and PVP was 0.005 g/mL, the transmittance of the complex system at each volume ratio was much lower than that of the component solutions, and when PMAA/PVP ranged from 9:1 to 1:9, the transmittance values of the complex systems were close to one another. When PMAA and PVP solutions were mixed at a higher concentration (0.02–0.06 g/mL), the transmittance of the complex system became lower and lower as PMAA/PVP ranged from 9:1 to 6:4, and when PMAA/PVP was 6:4 to 3:7, the transmittance of the complex system was lowest.

The measurements fit the macrophenomena well. When PVP and PMAA solutions were mixed at the higher concentrations (0.06, 0.04, and 0.02 g/mL), the macromolecular chains were curly, many macromolecular chains packed and reacted with one another (Scheme 1), and a gel substance deposited from the water phase. As a result, the transmittance of the complex system was lower than that of PMAA and PVP solutions. On the contrary, when PMAA and PVP solutions were mixed in diluted solutions (0.002 and 0.0005 g/mL), the macromolecular chains were more stretched, and they were wrapped by water molecules. The formation of hydrogen bonds between the

macromolecular chains and water molecules was easier than that between the macromolecular chains (Scheme 2). This showed higher transmittance, like that of the component solutions. During the experiment, we also found a strange phenomenon: when PMAA and PVP were mixed at 0.005 g/mL, a mass of white floccules was formed and suspended in aqueous media when PMAA/PVP ranged from 9:1 to 1:9, instead of a gel substance being formed or the solution state being maintained. Therefore, the transmittance of the complex system was much lower than that of other complex systems, reaching even about 3%. This phenomenon requires further study in the future.

The transmittance of the complex system was related not only to the concentrations of the component solutions but also to the volume ratios of PMAA to PVP. At certain concentrations, when PMAA/PVP ranged from 6:4 to 3:7, the molar contents of carboxyl groups in PMAA and carbonyl groups in PVP were close to each other (Table I), and these two groups interacted well with each other. Therefore, more hydrogen bonds were formed between the carboxyl and carbonyl groups, and many complexes came into being, weakening the interaction of the polymer with the water molecule and resulting in a decrease in the transmittance. At other PMAA/PVP volume ratios (9:1 to 7:3 and 2:8 to 1:9), the molar content of the carboxyl groups was quite different from the molar content of the carbonyl groups, and this resulted in more bare groups interacting with water molecules.

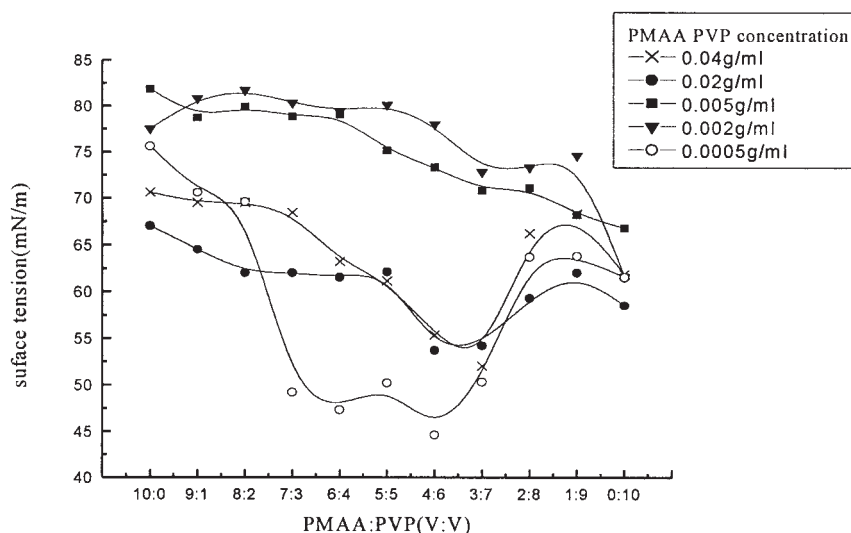
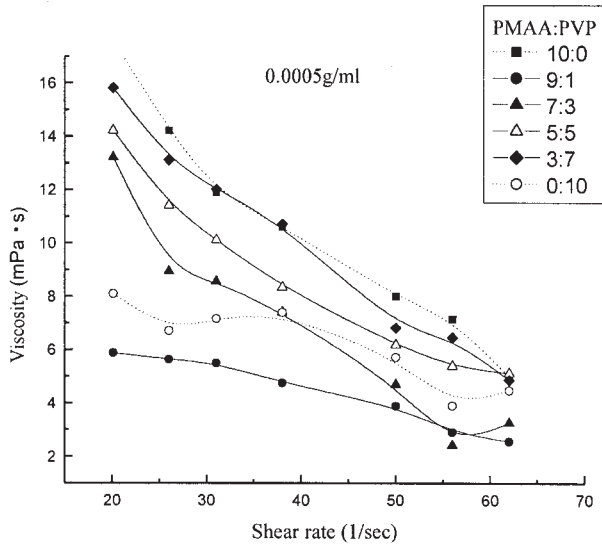
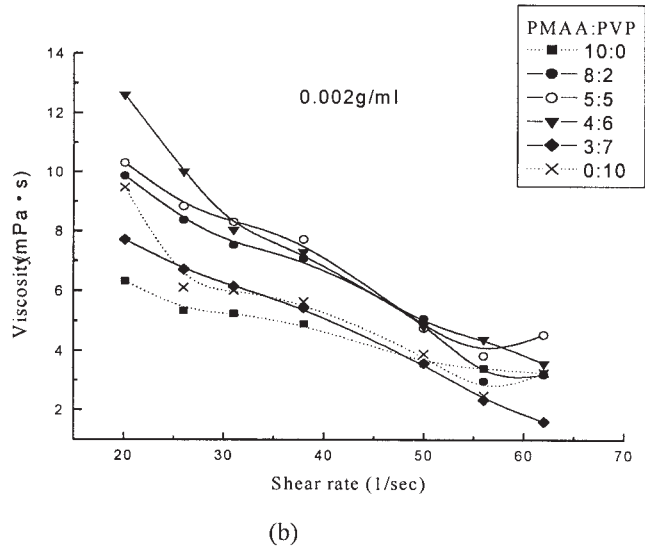


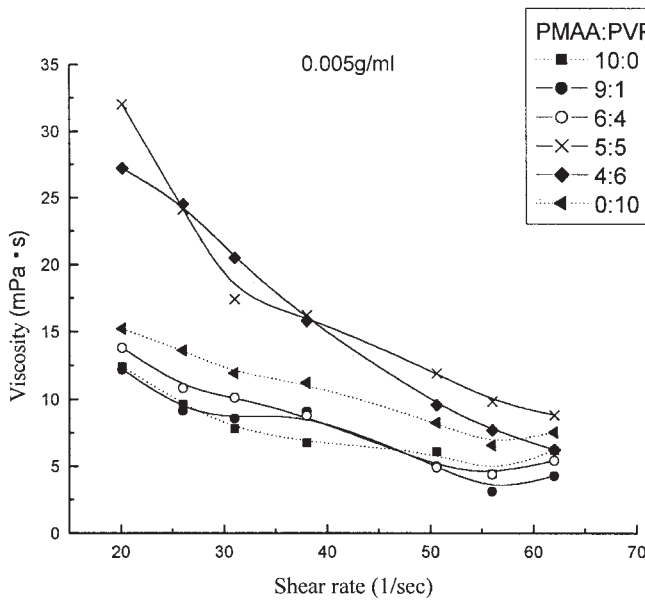
Figure 2 Variation of the surface tension of the complex system PMAA/PVP with the volume ratio at certain concentrations.



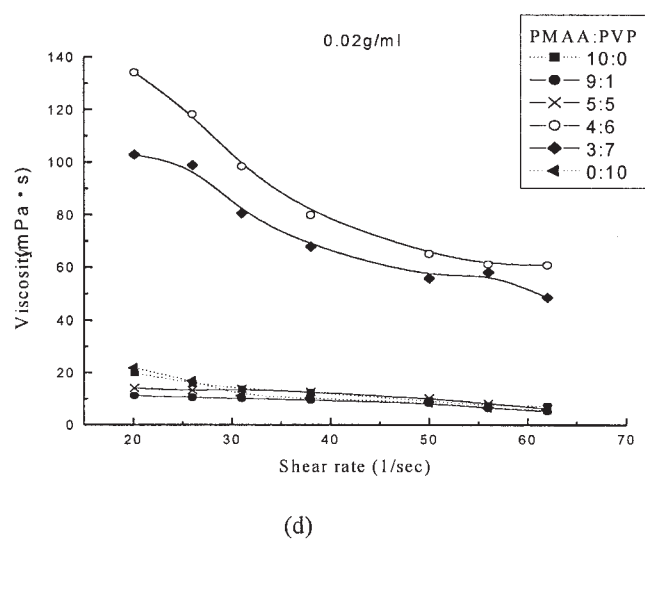
(a)



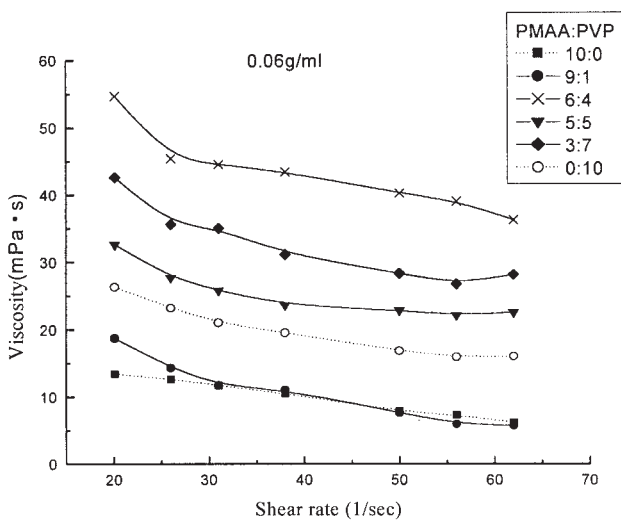
(b)



(c)



(d)



(e)



The transmittance of the complex system at these ratios was higher than that at other ratios.

#### Analysis of the surface tension of the complex system PMAA/PVP

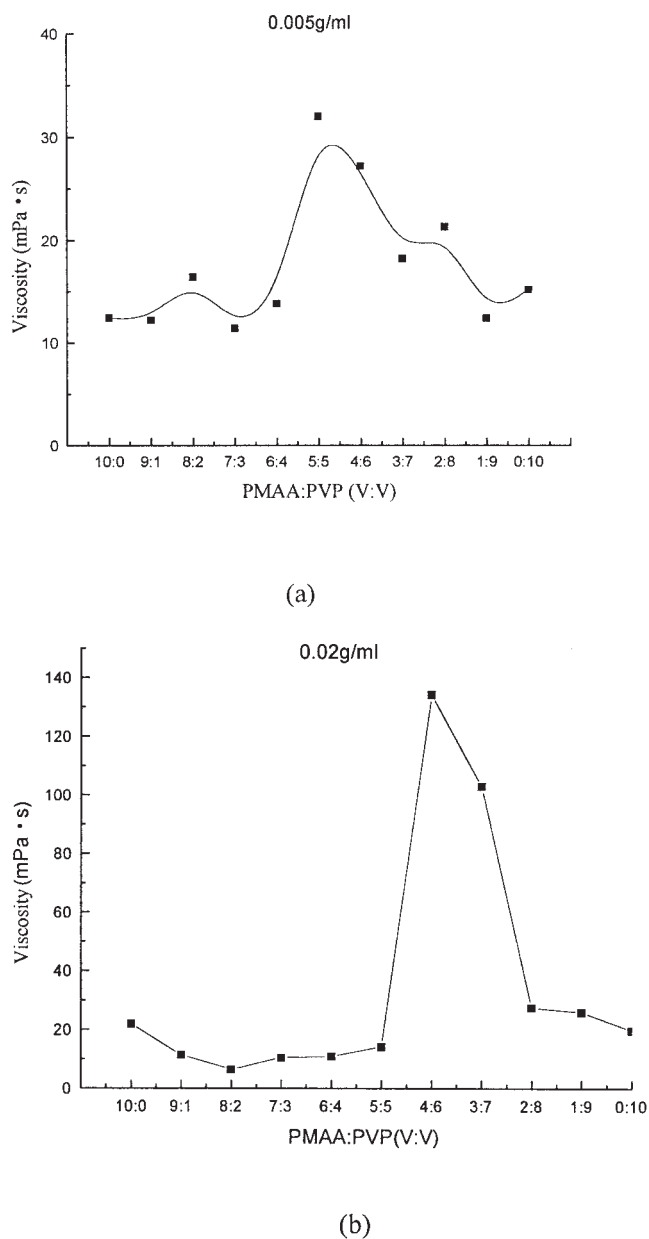
The polarity of the group is the important factor affecting the surface tension of a solution. In general, the surface tension increases with the polarity of the group.<sup>9</sup> When PMAA and PVP solutions were mixed together, the polarity of the complex system was weakened because of the interaction of side groups in the macromolecular chains, and this resulted in a decrease in the surface tension of the complex systems.

Figure 2 shows the variations of the surface tension of the complex systems with the volume ratio at certain concentrations of PMAA and PVP solutions. When PMAA and PVP solutions were mixed at 0.0005, 0.02, and 0.04 g/mL, the curves show similar trends. When PMAA/PVP ranged from 9:1 to 5:5, the surface tension of the complex system fell first and then reached its lowest value when PMAA/PVP ranged from 4:6 to 3:7. This indicates that at these volume ratios, the carboxyl and carbonyl groups interacted with each other more completely than at other ratios. When the concentrations of the component solutions were 0.005 and 0.002 g/mL, the surface tension of the complex systems obtained at each volume ratio was close to that of the component solutions, and this indicates that the surface tension was related to the volume ratio and concentration of the component solutions. This phenomenon needs more research.

#### Analysis of the viscosity of the complex system PMAA/PVP

The relationships of the viscosity with the shear rates, volume ratios, and concentrations are shown in Figures 3–5, respectively. When the concentration of the component solutions and the volume ratios were certain, the curves show similar trends; that is, the viscosity of the component solutions and complex systems decreased as the shear rate increased. When the concentration of the component solutions (e.g., 0.0005 and 0.002 g/mL) and the shear rate (e.g.,  $20.1 \text{ s}^{-1}$ ) were certain and when PMAA/PVP was 6:4–3:7, the viscosity of complex systems was higher than that of complex systems obtained with other ratios. The variations of the viscosity with the concentration at certain volume ratios and shear rates is shown in Figure 5; the two curves show analogous trends. When the concen-

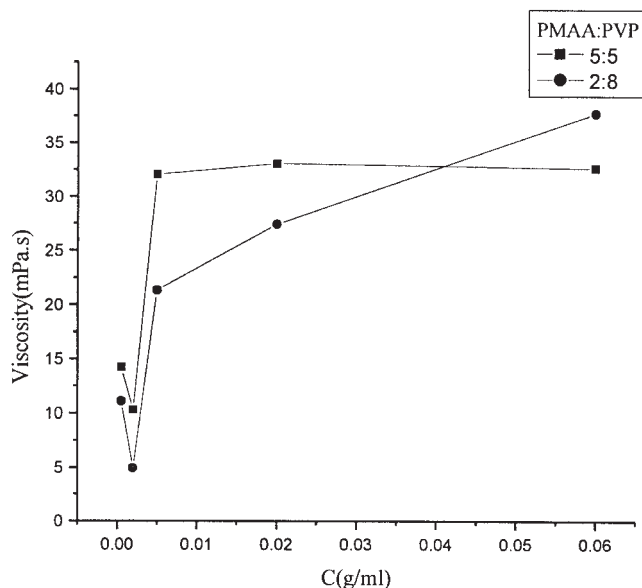
**Figure 3** Variation of the viscosity of the complex system PMAA/PVP with the shear rate at certain concentrations and volume ratios. The concentrations were (a) 0.0005, (b) 0.002, (c) 0.005, (d) 0.02, and (e) 0.06 g/mL.



**Figure 4** Variation of the viscosity of the complex system PMAA/PVP with the volume ratio at certain concentrations (shear rate =  $20.1 \text{ s}^{-1}$ ). The concentrations were (a) 0.005 and (b) 0.02, g/mL.

trations of the PMAA and PVP solutions were 0.0005–0.002 g/mL, the viscosity fell, and then the viscosity of the complex systems increased sharply from 0.002 to 0.005 g/mL; in the end, the viscosity changed little from 0.005 to 0.06 g/mL.

The experimental results show that at a certain volume ratio of the component solutions and at a certain shear rate, when the PMAA and PVP solutions were mixed at a higher concentration (e.g., 0.06 or 0.02 g/mL), the macromolecular chains were curly and packed with each other; this caused an agglomerate gel substance. The viscosity value actually showed the



**Figure 5** Variation of the viscosity of the complex system PMAA/PVP with the concentration at certain volume ratios (shear rate =  $20.1 \text{ s}^{-1}$ ).

viscosity of gel substances, and so the viscosity was much higher than that of the complex systems obtained at lower concentrations (e.g., 0.002 and 0.0005 g/mL). When PMAA and PVP were mixed at 0.005 g/mL, gel substances were not formed, but many small and white floccules were obtained, which made movement of the macromolecule difficult in the solvent; therefore, the viscosity of the complex was also higher than that of the complex systems obtained at 0.002 and 0.0005 g/mL. When the PMAA and PVP solutions were mixed at concentrations of 0.002 and 0.0005 g/mL, the complex systems always remained in the solution state, but the viscosity of the complex system obtained at 0.0005 g/mL was a little higher than that of the complex system obtained at 0.002 g/mL. A polyelectrolyte effect of PMAA caused this result.

When PMAA and PVP solutions of certain concentrations were mixed in different volume ratios, the

viscosity was also different. At higher concentrations, that is, 0.06, 0.02, and 0.005 g/mL, when PMAA/PVP ranged from 6:4 to 4:6, the molar contents of the carbonyl and carboxyl groups were close to each other (Table I), and this caused more gel substance or small floccules to be formed, so the viscosity of the complex system at these volume ratios was higher than that at other volume ratios. In addition, at lower concentrations, that is, 0.002 and 0.0005 g/mL, the macrophenomenon was always the solution state being kept at each ratio, but the viscosity of the complex system obtained at 6:4–4:6 ratios was also higher than that at other ratios. This indicated that at these ratios, more macromolecules reacted with one another, and molecular chains were lengthened and enlarged; this resulted in the viscosity rising.

## CONCLUSIONS

The properties of the complex system PMAA/PVP are related not only to the ratios of the component solutions but also to the concentrations of the component solutions. Intermacromolecular complexation is a new way of forming new materials and can be used in many special fields.

## References

1. Chui, Y. D.; Yi, G. B. *Polymerization and Application of Polyvinylpyrrolidone*; Science Technology Literature Press: Beijing, 1995.
2. Yang, Y. L.; Xu, G. Y. *Shan Dong Univ Trans Nat Sci Ed* 2000, 35, 315.
3. Yuan, Y. M.; Wu, M. Y. *Polym Trans* 1996, 4, 480.
4. Yang, Y. L.; Luan, Y. X.; Peng, B. *Chem Phys Trans* 2002, 15, 141.
5. Peng, W. M.; Yu, H. N. *Jiang Han Univ Trans* 1997, 14, 50.
6. Liu, S. X.; Fang, Y.; Hu, D. D.; Gao, G. L. *J Appl Polym Sci* 2001, 82, 620.
7. Polacco, G.; Cascone, M. G.; Petarca, L.; Peretti, A. *Eur Polym J* 2000, 36, 2541.
8. Abdiev, K. Z.; Zhursumbaeva, M. B.; Khusain, S. K. *Kolloid Zh* 2001, 63, 850.
9. Cheng, C. X. *Chemical Physics of Surfaces*; Science Technology Literature Press: Beijing, 2001.